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**A NEW METHOD OF DETERMINING ACID BASE STRENGTH DISTRIBUTION
AND A NEW ACIDITY-BASICITY SCALE FOR SOLID CATALYSTS: THE
STRONGEST POINT, H_0**

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16. Abstract In this paper we illustrate our work using the strongest H_0 as an acid base scale. We concluded that the catalytic activity arises from carbonium ions for solid catalysts whose strongest point values are less than 2, from carbanions for solid catalysts whose strongest point value are larger than 10, and from both acid and base points for those which have the H_0 value of 4-8. Further, from correlation between selectivity of o-isopropyl compounds and the strongest point H_0 , we found that the ortho selectivity increased as the basicity of solid surface increased.			
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A Newer Method of Determining Acid Base Strength
Distribution and a New Acidity-Basicity Scale for Solid
Catalysts: the Strongest Point, $H_0^{1)}$

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I. Introduction

The acid base properties of solid catalyst surface greatly affect their catalytic activities. Therefore, it is important to quantify acid base properties of various solid surfaces. Further, it is significant to correlate those quantities with catalytic activities and selectivities, in order to understand catalytic mechanisms and to design new catalysts. The solid activities are often related to an acid or base point in a special strength range,²⁾ while the selectivity of a catalyst is correlated with overall acidity or basicity of the solid surface. Since there is no adequate physical quantity to express experimental acid base properties, for this purpose the electronegativity and partial charges have been used.³⁾

The activity of a solid surface can be expressed by the strength and number of the acid points (acid strength) and the basicity by the strength and number of the base points (base strength).²⁾ However, in most past work, the activity was expressed by the H_0 function (Hammett Deyrup acidity function⁴⁻⁶⁾), while the basicity was expressed by the H_- function. In other words, the acidity scale is different from the basicity scale for a single solid catalyst. Combining the titration method for acid distributions such as the Johnson method⁷⁾ and our titration method for base distributions, one can estimate and describe the acid base strength of a solid surface in a non-polar solvent using the H_0 function. Based on these, the authors derived a new scale for acid base strength, the strength point H_s .²⁾

2. Newer Method of Determining Acid Base Strength Distributions

The acidic strength of solid surface can be described by the H_0 function which represents the ability of solid surface which gives protons to a neutral base (indicator for measurement) absorbed on the solid surface and changes them to a

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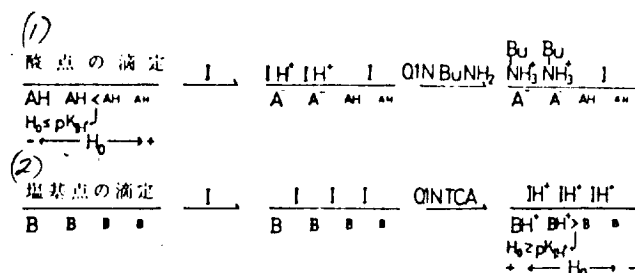


Fig. 1 Titration Principle

H_0 : the ability of an acid point to give I protons (acid strength H_0) or that of a base point to give I (conjugate acid) protons (base strength H_0),

AH: acid point, B: base point (The size of letters indicate the strength), $BuNH_2$: n butylamine, TCA: trichloro acetate, I: base indicator.

1. titration of acid point; 2. titration of base point.

conjugated acid.^{5,6)}

The amine titrations such as the Johnson⁷⁾ and Benesi⁸⁾ methods belong to this. Although there are various problems on this method, they are still utilized for characterizing acidic properties of the solid surface.^{9,10)} In Fig. 1 we present a process of this titration. If there are acidic points of $H_0 \leq pK_{IH^+}$ on the solid surface suspended in benzene, an absorbed indicator (I) turns into a conjugate acid (IH^+).

In the above, pK_{IH^+} represents a negative of logarithms of the dissociation constant for IH^+ . Now one can titrate the acidic points by use of more basic base (n butylamine) than the indicator, and then one can determine the amount of acids of $H_0 \geq pK_{IH^+}$ from the equivalent number of base consumed until the

acidic color (IH^+) disappears. Using Hammett base indicators of various pK_{IH^+} values, one can determine acidities of various strengths whose lower limits are H_0 . Then one can obtain relations between H_0 and acidity on the solid surface. This is a method of determining acid strength distribution.

1123

On the other hands, the amount of base points (basicity) is determined by a titration of non-polar suspensions with benzoic or acetic acids using bromthimol-blue and nitroaniline type as an indicator. It is expressed by the H_0 function which represents the ability to pull protons out from an acid indicator⁴⁾. This method can be used to describe base strength distributions only for strongly basic catalysts such as CaO and MgO or to measure basicity up to a certain strength.¹²⁻¹⁴⁾ Although there were a few reports that both acidity and basicity were measured for acidic and basic points on the same solid surface,^{15,16,17)} However, two scales are different for acidic and basic strengths.

The present authors described a value of the H_0 function for conjugate acids at the base point by the base strength H_0 .⁹⁾ No color change of the indicator I occurs, if there is no acid point of $H_0 \geq pK_{IH^+}$ on the solid suspended in benzene (see Fig. 1). By adding a standard acid solution (trichloro acetate) to it, the amount of basic points (basicity) for base strength $H_0 \geq pK_{IH^+}$ is determined. The end of this titration is a color change of I to IH^+ . The base strength is defined as the ability of conjugate acids, which are produced by an addition of protons from the acid standard solution to base points, to give protons to the indicator. This newer method of determining base points uses the same Hammett base indicators utilized for the titration of acid points, and the same H_0 function as a scale for acid base strength distribution. That is, by a combination of the traditional acid strength distribution and our new basic strength distribution

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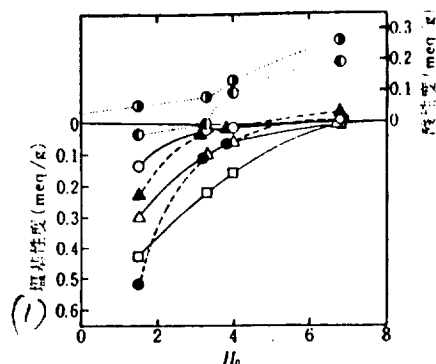


Fig. 2 Acid base strength distribution of almina (\circ), activated almina (Δ), γ -almina (\bullet), TiO_2 was thermally treated at 300°C (\square), and no treatment (\circ), and MgSO_4 ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was thermally treated at 300°C (\square) and 520°C (\circ)).^{18,19}

(activity: a sum of all points whose H_0 values are equal to or smaller than the value at the horizontal axis; basicity: a sum of all points whose H_0 values are equal to or larger than the value at the horizontal axis).

measurements, one can represent acid strength distributions of Al_2O_3 , ZrO_2 , and TiO_2 by the common scale of H_0 .⁸⁾ Some of our results are displayed in Fig. 2.

2. The Strongest Point H_0 and a Unified Scale for Acidity and Basicity

The acid strength distribution of solid catalysts is traditionally represented by the minimum acid strength H_0 , which is the smallest pK_{JH^+} value of the Hammett base indicators whose color change to acidic sides on the solid surface.¹⁷⁻¹⁹⁾

This was applied to solid acids using H_0 as a measure. On the other hand,

the base strength distribution was applied only a few solid bases using H_- as a measure.¹²⁾ The present authors determined acid base strength distributions of various solid compounds such as metal oxides, metal sulfates, metal tungstates. We found that the maximum H_0 value of the acid point is equal to that of the base point from each distribution. We define this H_0 value as the strongest point.¹³⁾ As seen in Fig. 2, both acidity and basicity are zero at H_0 . For all solid samples only one strongest point H_0 exists (see Fig. 2). It is noted that the strongest point H_0 is an only point which represents the strongest values for an acidic point and base point simultaneously.

When the H_0 value is large positive, the solid surface has strong base points and weak acid points, while when it is large negative, the surface has strong acid points and weak base points. In other words, the strong point H_0 is a physical measure of acidity and basicity of the solid surface. Further, the strongest point H_0 may also represent the strongest points of acidity and basicity of the solid surface which is partly covered by amine or acid standard solutions. In Fig. 3 various solids are listed in decreasing order of their H_0 values. Further, we add the traditional view of solid acid and base to Fig. 3.

Since the value of the strongest point H_0 is observable, they vary depending on the surface structure of solid as well as type of solid compounds.¹⁴⁾ The most significant factors on H_0 include water molecules of crystal water, hydroxides, number of protons, and their bonding states.^{2,20)}

4. Acid Base Strength Parameter Sensitive to Surface Structure, and Relation between Insensitive Parameter and the Strongest Point H_0

In Table I, we list various parameters which represent acidity and basicity of solid metal compounds and oxides. The electronegativity and partial charge

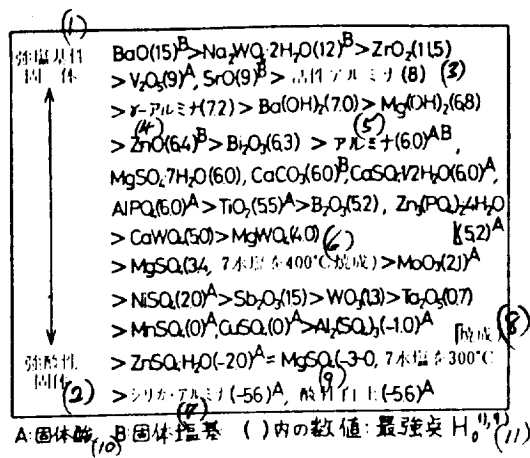


Fig. 3 Acidity and basicity order of various solids depending on their strongest point.⁽¹¹⁾

1. strongly basic solid; 2. strongly acidic solid; 3. activated alumina; 4. γ-alumina; 5. alumina; 6. SUIEN burned at 400°C; 7. silica: alumina; 8. SUIEN burned at 300°C; 9. acid clay; 10. A: solid acid, B: solid base; 11. figures in () represent the strongest point H₀⁽¹¹⁾

Table 1 Overall scales representing acidity and basicity of solid metals and oxygen compounds.

overall scale for acidity and basicity	Characteristics
partial negative charge of theoretical bonded oxygen (γ)	one value for each compound
electro negativity of a metal ion	theoretical one value for each valent state of metal
ZPC (equipotential point)	observed (aqueous solution); one value for each solid
the strongest point H_0 (H_{max})	observed (nonpolar solvent); one value for each solid

are independent of surface structures of solid; they are structurally insensitive parameters.^{23,22,19,21-24} Although they correlate with ZPC (zero point of charge)²³ and the strongest acid point H_0 ,^{19,21} such correlations are found only for the same kind of solids. For much wider ranges of solid, no correlation was observed. Further ZPC is sensitive to the surface structure but it is controversial since it is measured in colloidal suspension.^{23,25,26}

According to the homogeneity principle of electro negativity (Sanderson),²⁷ the bonding electrons tend to distribute toward a more electro negative atom than the other atom and all constituent atoms are nearly equal in electro negativity. For metal compounds and oxides the electro negativities of metal and oxygen atoms are equal to that of the molecule. Let S_{M+i} , S_{O+i} , and S_m be electro

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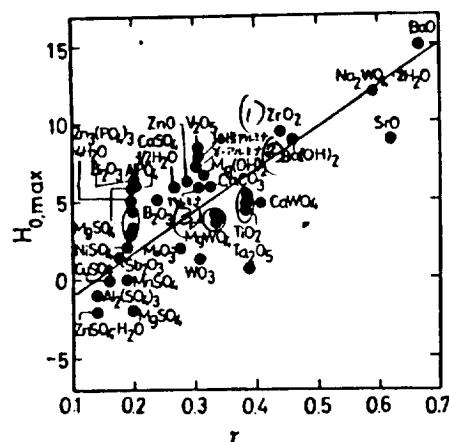


Fig. 4 Comparison of the strongest point H_0 ($H_{0,max}$) and partial negative charges (γ) of bonded oxygen.^{1,9)}

1. various almina; 2. γ -almina; 3. almina.

negativities of the metal atom whose partial charge is δ , of the oxygen atom whose partial charge is γ . Then the electro negativities is linear in γ :

$$S_m = S = S_o\gamma; S_o\gamma = 5.21 - 4.75\gamma. \quad (1)$$

We obtained a crude correlation between calculated values of γ and the strongest point H_0 , which is displayed in Fig. 4.⁹⁾ The larger the γ value and the smaller the electro negativity S_m , the more basic the solid surface is (scattering of H_0 values in Fig. 4 may be due to surface structure of solids). This is consistent with other findings, the smaller the electro negativity of metal ions, the larger the strongest point H_0 of solid metal sulfates²¹⁾ or solid metal oxides¹⁹⁾; the larger the difference in electro negativity of metal and oxygen atoms, the weaker the acidity of metal oxide surface and aqueous solution of oxides;²⁷⁾ further, the smaller X_0 , the weaker the acidity of metal ions.²⁸⁾

1124

Next we will discuss a relation between ZPC and the strongest point H_0 . Uncharged solid surfaces suspended in water have two conflicting properties: one (acid) is to become a negative in charge by releasing protons in water, the other (base) is to become a positive charge by acquiring protons from water.^{23,26} Difference between positive and negative charges on the solid surface varies with pH of the aqueous medium.

The schematic diagram of this variation is shown in Fig. 5. ZPC corresponds to the pH value at which the difference is zero. This relation looks similar to that between the acid base strength distribution and the strongest point H_0 , which is also displayed in Fig. 5. When the acidity is stronger on solid surface, ZPC is smaller, and when the basicity is stronger, ZPC is larger.^{23,26}

Experimental values^{25,29} of ZPC correlate with those of the strongest point H_0 as shown in Fig. 6. Observed deviations may be due to solvent effects on acidity or basicity of solid surface. ZPC is also affected by water in solid.^{25,30}

If ZPC and the strongest point H_0 are measured for the same sample (same amount of water on the solid surface), and if water and non-polar solvent contribute to the same degree to the H_0 function of each solvent surface, it is very likely that both surfaces have the same acidic and basic properties and the same value of H_0 . If the solid surface for ZPC measurement releases protons to the indicator I as much as the aqueous solution does to I, the equation (2)⁴⁻⁶,

$$H_{0,max} = ZPC + \log(f'_{III}/f'_I) \quad (2)$$

where $H_{0,max}$ and f' are the strongest point H_0 and an activity coefficient in aqueous medium. When the second term is neglected, $H_{0,max} = ZPC$.¹¹

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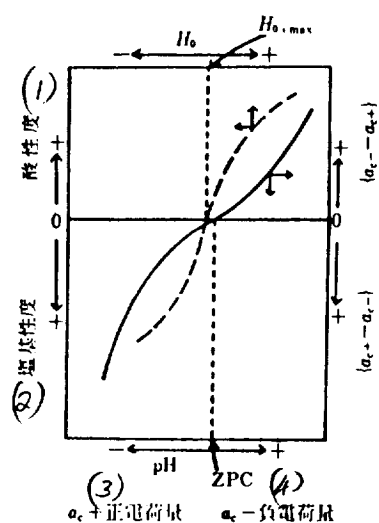


Fig. 5 Relation between the acid base strength distribution and the strongest point H_0 ($H_{0,max}$) and relation between pH and surface charge of an aqueous solution and ZPC.

1. activity; 2. basicity; 3. positive charge; 4. negative charge.

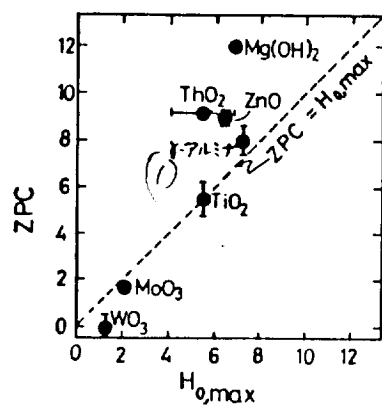
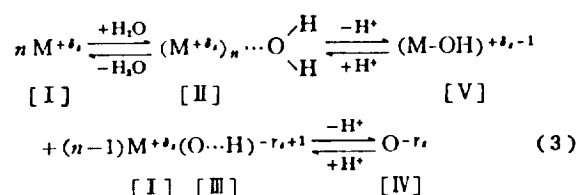


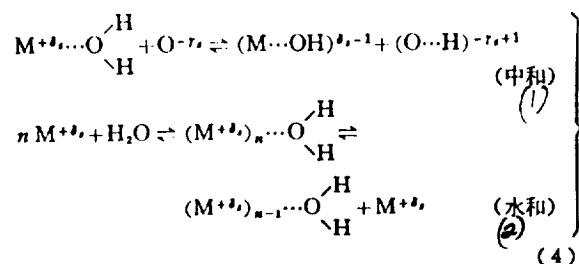
Fig. 6 Comparison between the strongest point H_0 ($H_{0,max}$) and ZPC.
1. γ -alumina.

5. Appearance of Acid Base Strength Distributions and the Strongest Point H_0

The acid point on solid compounds which contain oxygen and metal atoms consists of partially charged metal atoms (I)^{21,31-36}, I with coordinated water molecules (II; stoichiometric ratio $n = 1-2$),^{21,31,34,37} and negatively charged oxygen atoms (N) coordinated with protons (III).^{33,38,39} On the other hand, the base point is N^{40,41-43} or I with hydroxyl groups (V).^{36,42} These are produced by absorption and desorption of water and by coordination and dissociation of protons as shown in eq. (3). As a result, the acid-base strength distribution develops.



When the solid catalyst is prepared by precipitation, coprecipitation, or drying and burning the solid, protons, cations and anions can move in aqueous, water, or steam media and electrons in the solids can exchange positions fast enough that they can attain an equilibrium. Therefore there is only one strongest H_0 value for a solid surface. In other words, the acid base strength distribution with the strongest point H_0 and frequencies for acid and base points are determined by the equilibrium state given by eq. (4):



for eq. 4: 1. neutral; 2. hydration.

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6. Summary

The strongest point H_0 is one of the tools to understand acid base properties of solid surface. We below show our work using the strongest H_0 as a acid-base scale.

Liquid phase isopropyl reaction of m-cresol by propylene takes place with either solid acids or solid bases.^{44,45)} However catalytic activities and selectivities vary significantly from catalyst to catalyst. We carried out the reaction by using metal oxides, hydroxides, sulfides, sulfates, and tungstates and obtained a correlation between catalytic activity and the strongest point H_0 . We concluded that the catalytic activity arises from carbonium ions for solid catalysts whose strongest point values are less than 2, from carbanions for solid catalysts whose strongest point value are larger than 10, and from both acid and base points for those which have the H_0 value of 4 - 6.⁴⁵⁾ Further from correlation between selectivity of o-isopropyl compounds and the strongest point H_0 , we found that the ortho selectivity increased as the basicity of solid surface increased.⁴⁵⁾

We succeeded to design and develop metal sulfates/alumina catalysts which were superior in catalytic activities and ortho selectivities by applying our finding.⁴⁶⁾ These catalysts are acid base type.⁴⁷⁾ For polar solvent systems, values of the strongest point H_0 should be corrected by an effect of solvent. Alternatively, the H_0 value may be determined in polar solvents.

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